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SELECTIVE REMOVAL OF ORGANICS FOR WATER RECLAMATION

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SUMMARY

Electrooxidation is a means of removing organic solutes directly from waste waters without the use of chemical expendables. This research demonstrated the feasibility of the concept for oxidation of organic impurities common to urine, shower waters and space habitat humidity condensates. Electrooxidation of urine and waste water ersatz was experimentally demonstrated. This report describes the electrooxidation principle, reaction kinetics, efficiency, power, size, experimental test results and water reclamation applications. Process operating potentials and the use of anodic oxidation potentials that are sufficiently low to avoid oxygen formation and chloride oxidation are described. The design of a novel electrochemical system that incorporates a proton exchange membrane (PEM) electrolyte is presented based on parametric test data and current fuel cell technology.

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INTRODUCTION

The success of permanent human presence in extraterrestrial space environments such as the moon and Mars will require closed regenerative life support systems that demonstrate self-sufficiency, reliability, and longevity without the use of expendables. Reclamation systems for potable and hygiene water use must recover all water from wastes. New proven technologies are needed that provide for removal of organic impurities common to waste waters and also provide disinfection features.

Electrochemical oxidation of waste waters is a proven method for removing organic impurities and was demonstrated in a breadboard electrolysis/electrodialysis water reclamation system for processing urine by Putnam and Vaughan (1). The organics in urine were oxidized in the electrolyzer and the inorganic salts were removed by electrodialysis. However, the electrolyzer was operated at a high potential and oxygen and chlorine were generated forming an insoluble potassium perchlorate salt. Lockheed (2) performed similar work and investigated a variety of electrodes including a Pt/Rh electrocatalyst. Yao *et al* (3,4) showed that with controlled potentials, urea can be electrochemically oxidized at potentials less than the standard potential for chlorine formation (i.e., <1.34 V vs. the Normal Hydrogen Electrode). However, the urea oxidation rates were relatively slow per unit area of electrode surface, thus, necessitating the use of electrodes with high surface areas to obtain substantial rates of oxidation. Appleby et al (5) showed that Ru/Ti oxide could be used for the electrolysis of solutions representative of artificial kidney dialysate (NaCl + urea) to produce N_2 and CO_2.

This paper discusses the merits of treating urine directly by electrochemical oxidation with controlled potentials where chlorine is not generated, perchlorates are not formed, and water oxidation is limited. The electrooxidation technique shows potential for the post-treatment of other reclaimed waste waters (distillates, reverse osmosis permeates, and habitat humidity condensates). However, a non-expendable electrolyte is needed for the process. The current research is pursuing use of a cation-exchange membrane as used in fuel cell technology. This approach is presented with parametric test data and a design of a post-treatment electrooxidation module. The reaction kinetics and the principle of the electrooxidation process are presented.

METHODOLOGY

An electrochemical cell (Figure 1) used for the experiments consisted of a glass compartment (80 ml volume) surrounded by a glass water jacket. An air-tight seal was made between the cover and cell using a rubber "o" ring. The cover contained fittings for a gas inlet, a Ag/AgCl reference electrode and a thermometer. Two wires 0.5 mm in diameter were extended through the cover and fitted with connections to the working and counter electrodes. Both these electrodes are high surface area platinized platinum gauze electrodes that are cylindrical in configuration. The outer of the two electrodes has a diameter of approximately 2.5 cm and a height of 3 cm while the inner electrode has the same height but a slightly smaller diameter so it could fit inside the former electrode.

Ultrasonication was employed during the platinization process as a means of increasing the electrode durability (see 6). Smooth platinum gauzes were formed into cylinders (geometric area approx. 60 cm^2) using a spot welder. Before platinization, the electrodes were cleaned in hot aqua regia for 10 minutes. After thorough washing with distilled water, the electrodes were transferred to a 100 ml glass beaker containing chloroplatinic acid/lead acetate solution (1.5% $PtCl_6^{2-}$) and 0.02% Pb^{2+}) in 1 M HCl. The beaker was suspended in an ultrasonic bath (Bransonic). The cylindrical shaped gauze to be platinized was placed in the center of the beaker and a platinized platinum electrode was placed around the inside wall of the beaker. To prevent the two electrodes from contacting each other during the platinization, a nylon mesh separator was used. Connections were made to a Princeton Applied Research 173 potentiostat/galvanostat. At the same time as the onset of the current, the ultrasonic bath was switched on. Current was applied at 50 mA for 30 minutes followed by 30 minutes at 100 mA. The current was stepped to 800 mA for a further 1.5 hours. The newly platinized electrode was washed and then its area was measured using the procedure given above. Roughness factors in excess of 500 were achieved. Platinum black electrodes were made in this way to enhance their durability. A Nafion 117 cation exchange membrane (thickness 0.2 mm) was tightly fitted between the inner and outer electrodes. The membrane was prepared as the Na^+ form which involved first cleaning the membranes by boiling in dilute H_2O_2 followed by several boiling steps in millipore water. The membranes were then boiled in 1.0 M NaOH to give the sodium ion form of the membrane followed by boiling three times in millipore water. The above arrangement was modified in the experiments to obtain current-voltage relationships. One of the platinum gauzes was removed and a smooth platinum wire working electrode was inserted through an opening in the cell cover. The membrane was also removed.

The platinum working electrode surface areas were determined by obtaining cyclic voltammograms in 1 M sulfuric acid and determining the charge associated with the adsorption of the hydrogen monolayer on the electrode surface (6). The experiments performed with urine did not require addition of an electrolyte since urine contains adequate electrolytes for the electrooxidation process. In all the other experiments, a 1 M sodium perchlorate ($NaClO_4$) solution was used. Stirring was effected using a magnetic follower. The electrode potential was maintained at a predetermined value using a potentiostat. A coulometer was used to measure the charge comsumed.

Experiments were performed to obtain current-voltage relationships (Figure 2). Tests were performed to establish the reaction kinetics (Figures 3-6), to examine the pH effects on the urea oxidation (Figures 7 and 8) and to obtain an electrooxdation profile of urea, urine and the cocktail mix (Figure 10-14). Urea was selected for the experiments over other organic impurities because of its prevalence in all waste waters and because the compound is difficult to oxidize. The cocktail mix (Table 2) contains organics common to reclaimed waste waters (urine distillates, wash water, permeates and humidity condensates) and was the baseline test solution used in previous studies (7).

The organic and inorganic carbon measurements were performed on an Oceanographic Inc. instrument. Total nitrogen was measured by the Kjeldahl method and was performed to track the organic nitrogen content during the electrooxidation experiments. Chloride was measured for tracking salt content. The pH was measured to observe its effects on the kinetics of the electrooxidation process and also to observe the hydrogen ion concentration during the oxidation process. The number of viable microorganisms was determined by standard plate counts.

RESULTS

The electrochemical behavior of urea was determined over a broad potential range. Cyclic voltammograms were recorded in aqueous 1 M $NaClO_4$ solutions, both with and without 1.0 M urea using a smooth platinum wire electrode. The voltammetric profiles are presented in Figure 2. The voltammetric profile of the supporting electrolyte alone exhibited the following characteristics: (1) peaks associated with the electrochemical desorption of a hydrogen monolayer from -0.82 to -0.10 V (NHE); (2) oxide film growth from a potential of about +0.35 V (NHE) to 1.15 V (NHE) with further oxide growth accompanied at more positive potentials by oxygen gas evolution; (3) the well-known hysteresis between oxide film formation and reduction on the reverse cathodic sweep; and, (4) adsorption of a hydrogen monolayer and hydrogen gas evolution at around -0.82 V (NHE).

Significant differences were observed between the voltammetric profiles in the absence and in the presence of urea in solution. In the presence of urea, there was a considerable enhancement in the Faradaic current at potentials corresponding to the formation of the oxide film on platinum. An ill-defined peak at a potential of ca. 0.95 V to 1.0 V (NHE) indicates that the direct electrochemical oxidation of urea is occurring. An enhancement in the Faradaic current is maintained on into the oxygen gas evolution potential region. A series of similar voltammograms were performed over a range of urea concentrations. A plot of the peak current density, associated with the ill-defined peak at ca. 1.0 V (NHE), versus the concentration of urea in solution was linear. These characteristics provide evidence that the enhanced anodic Faradaic currents were indeed associated with the direct electrochemical oxidation of urea at the oxide-modified platinum electrode surface. In addition, there was a linear relationship between the peak current density versus scan rate for a fixed urea concentration in solution. This relationship strongly suggests that electron transfer processes associated with the direct electrochemical oxidation of urea are limited by the adsorption of urea onto the oxide-modified platinum electrode surface.

Examination of the cathodic potential sweeps recorded in urea-containing solutions (see Figure 2) reveals that the currents associated with oxide film reduction are considerably reduced. Further, at more negative potentials, enhancements in the Faradaic currents, over and above that involving hydrogen monolayer adsorption, are attributed to the direct electrochemical reduction of urea at the platinum electrode surface. The lower platinum oxide reduction currents, derived from urea-containing solutions, is indicative of the strong adsorption (chemisorption) of urea onto the platinum metal surface.

The voltammetric plots described above clearly demonstrate that there is a broad potential range existing for the direct electrochemical oxidation of urea in near-neutral solutions. The potential range extends from about -0.15 V (NHE) up to about 1.2 V (NHE) with significant interference from oxide film formation processes. At potentials more anodic than the latter, concomitant oxygen gas evolution takes place, along with urea oxidation.

Urea Oxidation Kinetics - The direct electrochemical oxidation kinetics of urea was studied using steady state log i-V plots obtained under the following conditions: (1) various concentrations of urea; (2) fixed 3 M urea concentration at various temperatures; and, (3) fixed 3 M urea concentration at different pH values. The establishment of log i-V curves for urea oxidation involved cycling the electrode potential between the limits of hydrogen evolution and oxygen evolution for several scans. This was followed by holding the electrode potential at the most negative value used (typically -0.2 V NHE) until the residual current reached a very low value (in the order of 0.1 mA). A preselected anodic potential was then applied and the steady state current was noted after ten minutes had elapsed. The procedure was repeated for each selected anodic electrode potential.

Log i-V plots for urea oxidation shown in Figure 3 display two potential ranges. A non-linear segment is obtained at potentials lower than 1.35 V (NHE) and a linear Tafel region was obtained at potentials more positive than this value. In the absence of urea, the measured Tafel slope for oxygen evolution was 200 mV decade^{-1}. This value increased to 350 mV decade^{-1} in the presence of urea in the 1 M - 10 M range. The dependence of the rate of oxidation on the concentration of urea added to the supporting electrolyte for three selected electrode potentials in the linear Tafel region is given in Figure 4. From the linear plots obtained, the current density showed a minimal dependence upon urea concentration (i.e., d log i/d log c = 0.35).

Log i-V plots for urea oxidation at various temperatures are presented in Figure 5. As in Figure 3, two characteristic regions were observed with respect to electrode potential. The linear Tafel regions again yielded a slope of about 350 mV decade^{-1} for urea oxidation. Arrhenius plots for this reaction for three selected potentials in the linear Tafel region are given in Figure 6. A mean activation energy value of 14.1 kcal mole^{-1} (58.92 kJ mole^{-1}) was calculated from the slopes of the linear plots obtained.

Log i-V plots for urea oxidation at various solution pH values are shown in Figure 7. The effect of pH is most prominent in the alkaline region. The linear Tafel regions also yielded slopes of about 350 mV decade^{-1}. The dependence of the reaction rate on solution pH for two selected potentials in the linear Tafel region is presented in Figure 8. From the linear portion of the resulting plots, a value of d log i/d pH = 0.20 was obtained.

Reaction Mechanism - The two distinct regions of the log i-V plots (Figures 3, 5 and 7) indicate that the electrochemical oxidation of urea proceeds by two different reaction pathways. One pathway operates at potentials more negative than 1.20 V (NHE) and the other participates at potentials more anodic than this value.

Over much of the lower potential range, the platinum surface is likely to be free of an oxide film. On the clean or partially clean platinum surfaces, the dissociative chemisorption of organic molecules is a well known phenomenon. Thus, it is likely that subsequent to urea adsorption, dissociation will occur to give adsorbed species that can be readily oxidized electrochemically in a series of one-electron transfer steps at potentials more negative than 1.20 V (NHE). For instance, adsorbed hydrazine-like intermediates, derived from the dissociative adsorption of urea, can readily be oxidized in the range of -0.2 to 0.2 V (NHE).

While dissociative chemisorption of organics may play a central role in urea oxidation in the lower potential range, it is likely to play an insignificant role at the high potential range because the electrode surface is oxide-covered. It is proposed at potentials more positive than 1.2 V (NHE) in near neutral solutions, the mechanism for the electrochemical oxidation of urea involves a chemical reaction between an electrochemically generated *adsorbed* radical species and an adjacent *adsorbed* urea molecule. While the nature of the electrochemically generated oxidizing species at the platinum oxide surface is uncertain, adsorbed radicals, such as OH_{ads} and O_{ads}, are likely candidates.

The proposed reaction scheme for the direct electrochemical oxidation of urea at the high potential regions is outlined in Equations [1] through [7]. Electrochemical regeneration of the adsorbed surface hydroxyl radical ($Pt - OH_{ads}$) facilitates the subsequent chemical reactions between the generated hydroxyl radicals and the partially oxidized adsorbed urea species.

$$Pt_{surface} + H_2O \rightarrow Pt - OH_{ads} + H^+ + e^- \qquad [1]$$

$$Pt_{surface} + H_2NCONH_2 \rightarrow Pt - H_2NCONH_{ads} \qquad [2]$$

$$H_2NCONH_{2ads} + OH_{ads} \rightarrow H_2NCONH + H_2O \qquad [3]$$

$$H_2NCONH_{ads} + OH_{ads} \rightarrow HNCONH + H_2O \qquad [4]$$

$$HNCONH_{ads} + OH_{ads} \rightarrow HNCON + H_2O \qquad [5]$$

$$HNCON_{ads} + OH_{ads} \rightarrow NCON + H_2O \qquad [6]$$

$$NCON_{ads} + OH_{ads} \rightarrow CO_2 + N_2 + H^+ + e^- \qquad [7]$$

Evidence in support of this hypothesis is the high value of the Tafel slope calculated from log i-V plots in the presence of urea (350 mV decade^{-1}) compared to that obtained in the absence of urea (200 mV decade^{-1}). It is postulated that more than one intermediate oxidizing species is formed electrochemically on the oxide-covered platinum surface (e.g., OH_{ads} and O_{ads}). While both of these strongly oxidizing intermediates can take part in the oxygen evolution reaction only one of them (e.g., OH_{ads}) participates to any significant extent in organic electrooxidations. Thus, assuming similar surface coverages of OH_{ads} and O_{ads} and that a chemical reaction involving a surface OH_{ads} species and urea is rate determining, the current (or rate) for the urea electrochemical oxidation reaction will not increase as rapidly with increasing electrode potential, as would the oxygen evolution reaction. This phenomenon was indeed observed in the log i-V plots

Further evidence for the above mechanism comes from the very low dependence of the reaction rate on urea bulk solution concentration. An electrochemical oxidation pathway involving the direct electrode reaction of adsorbed urea with an adsorbed radical species, as proposed here, would require a zero reaction order with respect to bulk solution urea concentration. The observed reaction rate enhancements in alkaline solutions add further support to the above mechanism. Although the rate-determining step is unclear, it is assumed to be one of the reaction steps represented by Equations [3] through [6]. Thus, the higher surface coverages of Pt-OH_{ads} at alkaline pH would accelerate the chemical rate-determining step, as represented by Equations[3] through [6].

Periodic Reversed Pulse Electrolysis (PRPE)

Urea is the main component of urine (see Table 3) and its removal is an important step in the recovery of potable water. The feasibility of urea removal by direct electrooxidation at controlled potentials was examined using test solutions containing urea at 0.1 M urea (equivalent of 1200 ppm TOC) and 1.0 M $NaClO_4$ as the supporting electrolyte. Preliminary electrolysis studies demonstrated that the rates of urea oxidation were impractically low.

To overcome this limitation, periodic reversed pulse electrolysis (PRPE) was employed. This current reversal technique involves first applying a positive electrode potential (versus a Ag/AgCl reference electrode) to the outside platinum electrode which acts as the anode. After a predetermined period, a relay in combination with a timer, positioned in the electrical circuit as shown in Figure 9, reverses the direction of the current into the cell. Thus, the inside electrode acts as the anode while the outside electrode acts as the cathode. Within a few seconds after switching the roles of the electrode, the new anode regaines the applied anodic potential. Thus, the roles of the platinized platinum electrodes were periodically reversed between anode and cathode. The switching mechanism was constructed with 2 electronic timers and relays. Figure 10 demonstrates the extent to which PRPE enhances urea removal at a controlled potential of 1.4 V (NHE) compared to the situation where PRPE was not used. Using PRPE, the final TOC value was 1.0 ppm indicating that practically all the urea had been oxidized. Figure 11(a) shows the current versus time profile for urea oxidation in the absence of PRPE. In this case, the urea oxidation current decays rapidly to low steady state values after only a few minutes of electrolysis. The effect of PRPE performed at 1 minute intervals on the urea oxidation current is shown in Figure 11(b). The oxidation current remains high since, at a point before the low steady state oxidation current is reached, the electrolysis is restarted at a high rate on a new electrode.

Urea removal was also effective at 1.3 V (NHE) using PRPE at 1 minute intervals. A urea removal rate of 1.87 mg/hr/m^2 was achieved (electrode areas were determined by the hydrogen adsorption method). Additionally, if the time interval between switching the roles of the electrodes was decreased to 20 seconds, the urea removal rate increased to 5.26 mg/hr/m^2. This characteristic indicates that further optimizing the frequency of PRPE will be beneficial for follow-on work on a breadboard system.

Additional experiments were then conducted to assess the effect of chloride ions on the rate of urea oxidation in a perchlorate-based electrolyte. The results are shown in Table 1. In each experiment the final TOC values were 1 ppm, indicating that even in the presence of Cl^- in the concentration range found in urine (1,870 to 8,400 mg / l) controlled potential oxidation, in combinbation with PRPE, is effective for urea removal.

Electrooxidation of Raw Urine and Disinfection Studies

The experiment shown in Figure 12 was performed to assess the effect of PRPE on the purification of raw urine (see Table 3). Urine was electrolysed on high surface area platinized platinum electrodes. The electrode potential was 1.3 V (NHE) to avoid chlorine formation; the PRPE frequency was 1 minute. Samples of the treated urine were taken at intervals and the TOC and TKN levels were recorded as a function of the charge used in the electrooxidation. At the start of electrolysis there was some frothing due to relatively large amounts of gas formation. After 5×10^4 Coulombs were passed, there was no odor and the solution was clear. The resulting electrolyte consisted of very low levels of TKN indicating near total urea removal. The TIC levels were less than 1 ppm. The final values of TOC was 350 mg/L. However, continuing the electrolysis beyond this point was impractical due to the loss of electrode material. This experimental data, however, demonstrates the feasibility of urine pretreatment at low potentials for potable water recovery.

The results of 2-stage electrolysis are shown in Figure 13. Raw urine was collected and "spiked" with a bacterial sample from a pure culture of Escherichia coli. At the start of the electrolysis, the urine sample contained 1.2×10^8 viable bacteria/ml. Initially, a potential of 1.75 V (NHE) was applied. After 4 hours of electrolysis no viable bacteria were detected in the treated urine. However, in a urine sample that had been "spiked" with an equivalent bacterial concentration but had not been subjected to electrolysis, the bacterial level remained at 1.0×10^8 bacteria / ml after 4 hours. The final part of the electrolysis was performed at 1.3 V utilizing PRPE at 1 minute intervals. This experiment demonstrated the disinfection capabilities of electrochemical urine pretreatment. Additional advantages of the two stage approach are: (1), oxidants from chlorine production enhance the rates of oxidation over the first part of the electrolysis, thereby, decreasing the electrolysis time; and, (2), chlorates and perchlorates can be avoided by utilizing low potential direct oxidation during the final stages of the electrolysis.

Current Efficiency for Urine Electrolysis - It has been shown that the mixture of organics in urine can be approximately represented by the equation $C_2H_6N_2O_2$ (1). The equation for the electrochemical oxidation of this mixture is:

$$2H_20 + C_2H_6N_2O_2 \rightarrow N_2 + CO_2 + 10H^+ + 10e-$$

Using this equation and from calculating the amount of $C_2H_6N_2O_2$ oxidized from the TOC data, the current efficiency for first part of the electrolysis shown in Figure 12 (i.e., up to 3.14 x 10^4 Coulombs had been passed) is as follows:

Amount $C_2H_6N_2O_2$ oxidized = 0.012 moles

$$\text{Assuming 100\% current efficiency} = \frac{3.14 \times 10^4}{10 \times 9.648 \times 10^4}$$

$$= 0.032 \text{ moles}$$

$$\text{Current Efficiency} = \frac{0.012}{0.032} = 37.5\%$$

Electrooxidation of Simulated Reclaimed Water

An additional aim of this research was to assess the extent that electrooxidation technology used for urine treatment could be adapted for the post-treatment of reclaimed water. The success of this approach rests ultimately on the development of an electrolyzer that utilizes an ion conducting membrane to effect the electrooxidation of organics in water of low ionic content. However, an assessment of the feasibility of this approach for organic oxidation was made by adding an electrochemically inert liquid electrolyte (1.0 M $NaClO_4$) to the simulated waste water to provide the necessary ionic conductivity. The test solution contained simulated waste water (Table 2) having a concentration equivalent to 56 ppm TOC. The electrolysis was conducted over a range of electrode potentials on platinized platinum electrodes. The current was reversed at 1 minute intervals exactly as in the experiments on urine electrooxidation. Samples were taken periodically to determine the TOC levels.

Figure 14 shows that at the lowest potential used (1.2 V NHE), the TOC level decreased to the 2-3 ppm level but failed to attain lower values even upon prolonged oxidation. Stepping up the potential to 1.4 V (NHE) resulted in final values of 1 ppm. At 1.6 V (NHE) the final TOC value was 1 ppm; however, the charge consumed in achieving this value was greater than at 1.4 V (NHE) because of increased competition from oxygen gas evolution. When the electrooxidation was performed at 1.8 V (NHE), the final TOC level was 500 ppb. At this potential oxygen evolution was vigorous; hence, charge consumption increased significantly. These results indicate that high electrooxidation potentials are most effective for providing high quality water.

DISCUSSION

Urine Pretreatment - The primary research work carried out has demonstrated the feasibility of utilizing direct electrochemical oxidation as a means of urine pretreatment. The electrochemical formation of dissolved chlorine and its oxidation products (chlorates and perchlorates) are avoided. This approach is advantageous for the recovery of potable water.

The electrode kinetic study indicates that at a potential of 1.3 V (NHE) the direct oxidation of urea (and other organics) is achieved predominantly through the generation of adsorbed hydroxyl radicals that are confined to the platinum surface. Urea is difficult to oxidize largely due to the resonance interactions of the lone electron pairs on the nitrogen atoms with the adjacent carbonyl group. This can give rise to homogeneous rate constants orders of magnitude lower than those of other organic compounds on reacting with hydroxyl radicals (and other radical species) in aqueous solutions. Although the heterogeneous oxidation of urea by hydroxyl radicals on an electrode surface should facilitate higher reaction rates, due to urea intramolecular bond weakening as a result of chemisorption, the measured activation energy, 14.1 kcal mole^{-1} (cf., Figure. 6), indicates that even under these conditions the chemical oxidation reaction is sluggish.

Through the use of PRPE the apparent low rates of electrochemical urea oxidation can be overcome. Two hypothesis can be put forward to explain this effect. Since during PRPE the oxide layers are periodically reformed, increases in the surface concentration of OH radical oxidizing species may be observed.

Secondly, the technique favors transient electrolysis over steady state electrolysis. This latter effect is most clearly shown in Figure 11 where PRPE avoids the sluggish steady state rate of urea removal by maintaining the reaction in the high current density initial phase of oxidation. Yao and colleagues (3,4) also utilized a potential reversal technique for enhancing urea oxidation. In this work, urea oxidation was performed at a significantly lower potential (0.8 V NHE) that was used here and the electrodes were periodically subjected to cathodic treatments. At this lower potential, urea is oxidized by the dissociate chemisorption mechanism rather than through the generation of hydroxyl radicals. Thus, the effect of the cathodic treatments employed by Yao and colleagues can adequately be explained by the removal of the oxide layer. Cleaning or partially cleaning the platinum surface in this way provides an increased number of active sites on the electrode for the dissociative chemisorption of organics.

The energy requirements are a function of the current passed and the cell voltage (i.e., including the voltage drop due to the resistance between the anode and cathode). The voltage drop achieved a steady state value of around 1.5 V after 10 seconds following current reversal. In Figure 13, the total charge passed to treat 85 ml of raw urine was 1.4 x 10^5 Coulombs over a 125 hour period or the equivalent to 38.9 Amp-hr.

38.9 Amp-hr x 1.5 V = 58.4 W-hr / 85 ml of raw urine

= 687 W-hr / L of raw urine.

Post-Treatment Electrochemical Oxidation - The study shows that the electrooxidation of organics in reclaimed waters other than urine is feasible. It is likely that the mechanism of urea oxidation involves adsorbed hydroxyl radicals as described for urea oxidation where the enhanced effectiveness of utilizing higher electrode potentials could be due to increased surface concentrations of OH radicals.

The electrooxidation at 1.4V (NHE) required 2.6 x 10^4C in 132 hours or the equivalent of 6.6 A-hr. The cell voltage was 1.2V.

6.6 Amp-hr x 1.2V = 7.9 W-hr/70ml

= 113 W-hr/L (simulated waste water)

Platinum is more effective for oxygen formation than for organic oxidations. At 1.4 V (NHE) it is likely that large amounts of electrical energy are consumed due to oxygen formation.

For a post-treatment system, it will be necessary to design and develop a cell with a non-expendable electrolyte. A cation exchange membrane approach is proven for fuel cell technology and therefore shows merit for the electrooxidation of waste waters. A proposed electrochemical cell design concept is shown in Figure 15. In this system, catalytic electrodes are pressed onto both surfaces of the cation exchange membrane to form an intimate electrode-electrolyte assembly. The anode catalyzes the oxidation of organics in demineralized water. Protons are transported through the chemically resistant cation exchange membrane based on a perfluorinated polymer (e.g., Nafion®) and recombine electrochemically at the cathode to form hydrogen. Electrons pass through an external circuit. Improvements in this process can be made by: (1) developing electrocatalysts that are less effective for oxygen formation and yet are still effective for organic oxidations; and, (2) maximizing electrode surface area to increase oxidation sites on the electrode surface.

CONCLUSIONS AND RECOMMENDATIONS

This research study shows that electrochemical oxidation is a potential technology appropriate to pursue for water reclamation applications in space-based habitat environments. The research accomplished indicates the following:

1. Urine purification and disinfection can be achieved through the use of electrolyzers that employ controlled potential electrolysis at voltages less than that needed for chlorine generation.

2. Periodic reversed pulse electrolysis (PRPE) is a new process for enhancing rates of oxidation of organic impurities in waste waters (urine) with a potential for enhancing microbial disinfection.

3. Adsorbed hydroxyl radicals play an important role in urea oxidation on platinum oxide surfaces.

4. Electrooxidation shows potential for pretreatment of all waste waters and post-treatment for reclaimed waste waters but still remains to be totally demonstrated in a breadboard test system.

5. Feasibility of electrooxidation for post-treatment remains to be proven in a cation-exchange electrochemical cell system.

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Table 1 : Effect of Chloride on Urea Removal Rate.

Chloride Concentration (mg / l)	Electrode Potential (V/NHE)	Interval Between Potential Reversal	Rate of Urea Removal* (mg / hr / m^{2})
-	1.3	60	1.87
1,060	1.3	60	1.42
3,545	1.3	60	0.91
10,635	1.3	60	1.29

* Electrode areas used in the calculation were obtained by the hydrogen adsorption method.

Table 2 : Composition of Simulated Waste Water

Name	Formula	TOC (ppm)
Acetic acid	CH_3COOH	9
Benzoic acid	$C_6H_5CO_2H$	3
Benzyl alcohol	$C_6H_5CH_2OH$	3
Benzaldehyde	C_6H_5CHO	0.5
Caprolactam (2oxohexamethyleneimine)	$C_6H_{11}ON$	2
Ethanol	CH_3CH_2OH	2
2-Butoxyethanol	$CH_3(CH_2)_3OCH_2CH_2OH$	0.5
N-N-Dimethyl formamide	$HCON(CH_3)_2$	0.5
Octanoic acid	$CH_3(CH_2)_6CO_2H$	3
Phenol	C_6H_5OH	3
Cresol	$CH_3C_6H_4OH$	0.5
Propionic acid	$C_2H_5CO_2H$	9

TABLE 3. CONSTITUENTS OF HUMAN URINE EXCEEDING 10 mg/l

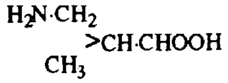
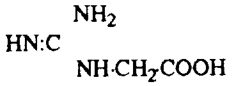
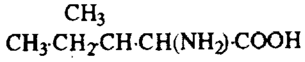
Item	Formula	Formula Weight	Range mg/l	mg/l
Total Solutes			36,700	46,700
Urea	H_2NCONH_2	60.1	9,300	23,300
Chloride	CL^-	35.5	1,870	8,400
Sodium	Na^+	23.0	1,170	4,390
Potassium	K^+	39.1	750	2,610
Creatinine	$C_4H_7N_3O$	113.1	670	2,150
Sulfur, Inorganic	S	32.1	163	1,800
Hippuric Acid	$C_6H_5CO\cdot NHCH_2\cdot CO_2H$	179.2	50	1,670
Phosphorus, Total	P	31.0	470	1,070
Citric Acid	$HOC(CH_2CO_2H)_2CO_2H$	192.1	90	930
Glucuronic Acid	$C_6H_{10}O_7$	194.1	70	880
Ammonia	NH_3	17.0	200	730
Uric Acid	$C_5H_4O_3N_4$	168.1	40	670
Uropepsin (as Tyrosine)	$HO\cdot C_6H_4\cdot C_2H_3(NH_2)\cdot CO_2H$	181.2	70	560
Bicarbonate	HCO_3^-	61.0	20	560
Creatine	$HN_2C(NH_2)N(CH_3)\cdot CH_2\cdot CO_2H\cdot H_2O$	149.1	0	530
Sulfur, Organic	S	32.1	77	470
Glycine	$NH_2\cdot CH_2\cdot CO_2H$	75.1	90	450
Phenols	C_6H_5OH	94.1	130	420
Lactic Acid	$CH_3\cdot CHOH\cdot CO_2H$	90.1	30	400
Calcium	Ca^{+2}	40.1	30	390
Histidine	$C_3H_3N_2\cdot CH_2\cdot CH\cdot (NH_2)\cdot CO_2H$	155.2	40	330
Glutamic Acid	$HO_2C\cdot CHNH_2\cdot (CH_2)_2\cdot CO_2H$	147.1	<7	320
Androsterone	$C_{19}H_{30}O_2$	290.5	2	280
I-Methylhistidine	$C_3H_3N_2CH_2(NH\cdot CH_3)\cdot COOH$	169.2	30	260
Magnesium	Mg	24.3	20	205
Imidazole Derivatives	$C_3H_4N_2$	68.1	90	200
Glucose	$C_6H_7O_6(COCH_3)_5$	390.4	30	200
Taurine	$NH_2\cdot CH_2\cdot CH_2\cdot SO_3H$	125.2	5	200
Aspartic Acid	$C_4H_7O_4N$	133.1	<7	170
Carbonate	CO_3^{-2}	60.0	100	150
Cystine	$[HO_2C\cdot CH(NH_2)\cdot CH_2S\cdot]_2$	240.3	7	130
Citrulline	$NH_2CONH(CH_2)_3\cdot CH\cdot (NH_2)\cdot CO_2H$	175.2	0	130
Threonine	$C_4H_9O_3N$	119.1	10	120
Lysine	$(NH_2)_2C_5H_9CO_2H$	146.2	5	110
Indoxylsulfuric Acid	$C_3H_7ON\cdot H_2SO_4$	231.2	3	110
m-Hydroxyhippuric Acid	$C_4H_4COHC(CONH\cdot CH_2COOH)$	195.2	1	100
p-Hydroxyphenyl- Hydrocrylic Acid			1	100
Aminoisobutyric Acid	 $H_2N\cdot CH_2$ $>CH\cdot CHOOH$ CH_3	103.1	3	120
Inositol	$C_6H_{12}O_6$	180.2	5	100
Formic Acid	$H\cdot CO_2H$	46.0	20	90
Urobilin	$C_{33}H_{40}O_6N_4$	588.7	7	90
Tyrosine	$HO\cdot C_6H_4\cdot C_2H_3(NH_2)\cdot CO_2H$	181.2	10	70
Pyruvic Acid	$CH_3\cdot CO\cdot CO_2H$	88.1	2	70
Albumin			7	70
Asparagine	$HO_2C\cdot CH(NH_2)\cdot CH_2\cdot CONH_2$	132.1	20	70
Tryptophan	$\underline{C_6H_4NH\cdot CH}:C\cdot C_2H_3(NH_2)CO_2H$	286.8	5	60
Ketones (as Acetone)	CH_3COCH_3	58.1	10	50

TABLE 3., cont.

Item	Formula	Formula Weight	Range mg/l	mg/l
Serine	$HO\cdot CH_2\cdot CHNH_2\cdot CO_2H$	105.1	20	50
Alanine	$H_2N\cdot CH(CH_3)\cdot CO_2H$	89.1	15	50
Purine Bases	$C_5H_4N_4$	120.1	0	50
Glycocyamine			15	45
Proline	$H\underline{N\cdot(CH_2)_3\cdot C}H\cdot CO_2H$	115.1	<7	40
Arginine	$H_2N\cdot C(:NH)\cdot NH\cdot(CH_2)_3\cdot CH(NH_2)\cdot CO_2H$	174.2	<7	40
Ascorbic Acid	$C_6H_8O_6$	176.1	3	40
Oxalic Acid	$HO_2C\cdot CO_2H$	90.0	1	30
Bilirubin	$C_{33}H_{36}N_4O_6$	584.7	3	30
Valine	$(CH_3)_2CH\cdot CH(NH_2)\cdot COOH$	117.2	<7	30
Phenylalamine	$\beta\cdot C_6H_5\cdot CH_2CH(NH_2)\cdot COOH$	165.2	6	30
Allantoin	$C_4H_7O_3N_4$	158.1	2	25
Oxoglutaric Acid	$C_5H_6O_5$	146.1	13	25
Leucine	$(CH_3)_2CH\cdot CH_2CH(NH_2)\cdot COOH$	131.2	8	25
Guanidinoacetic Acid	 $HN{:}C\begin{matrix}NH_2\\NH\cdot CH_2COOH\end{matrix}$	117.1	9	25
Isoleucine	 $CH_3\cdot CH_2\cdot\overset{CH_3}{CH}\cdot CH(NH_2)\cdot COOH$	131.2	4	22
Urobilinogen			0	17
Ethanolamine	$NH_2\cdot CH_2\cdot CH_2OH$	61.1	3	15
Guanidine	$(H_2N)_2C{:}NH$	59.1	7	13
Methionine Sulfoxide			0	13
Dehydroascorbic Acid	$C_6H_6O_6$	174.1	3	13
Other Organics				285

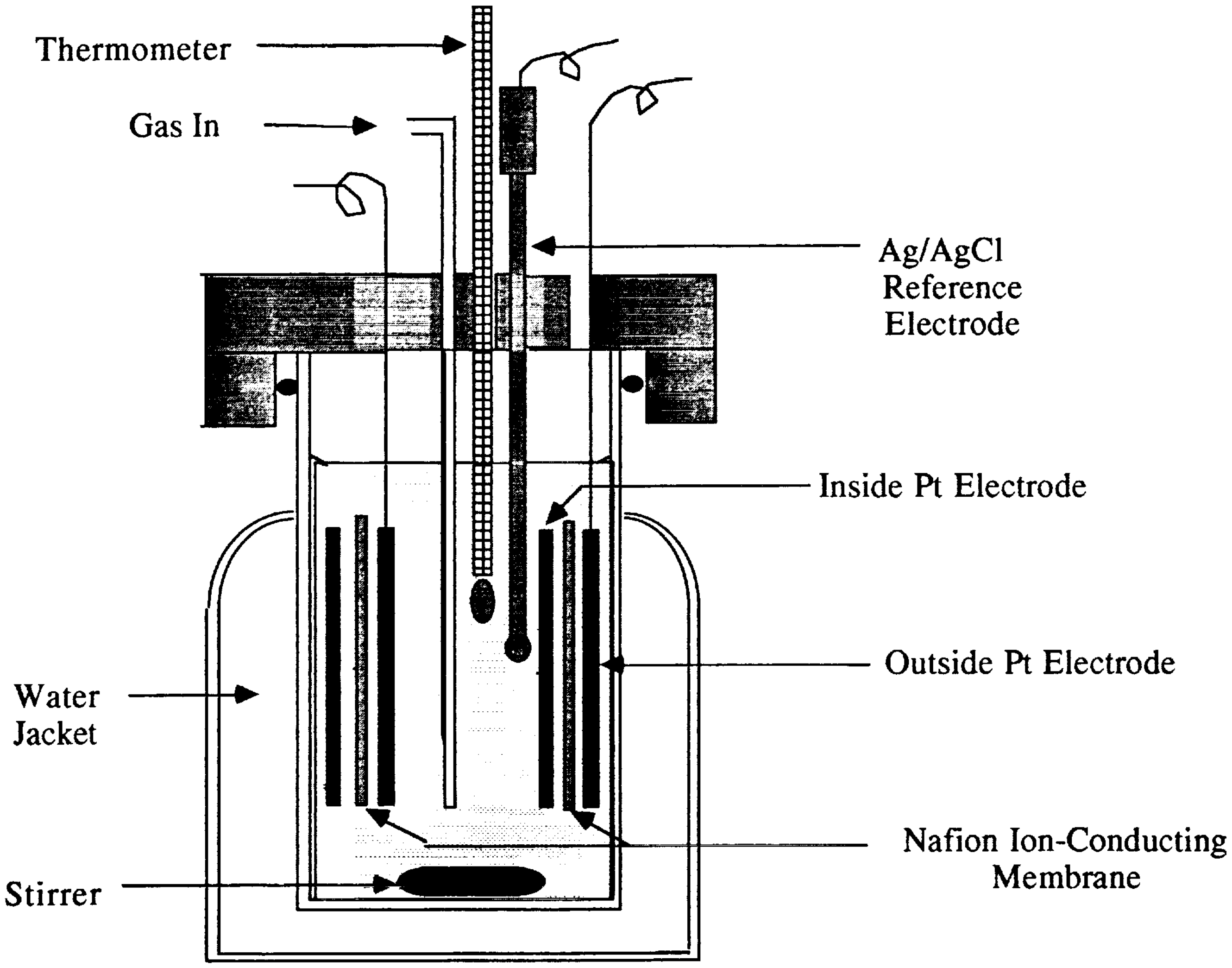

Thermometer
Gas In
Ag/AgCl Reference Electrode
Inside Pt Electrode
Outside Pt Electrode
Water Jacket
Nafion Ion-Conducting Membrane
Stirrer

Figure 1: Electrolysis Test Cell Incorporating an Ion-Conducting Membrane.

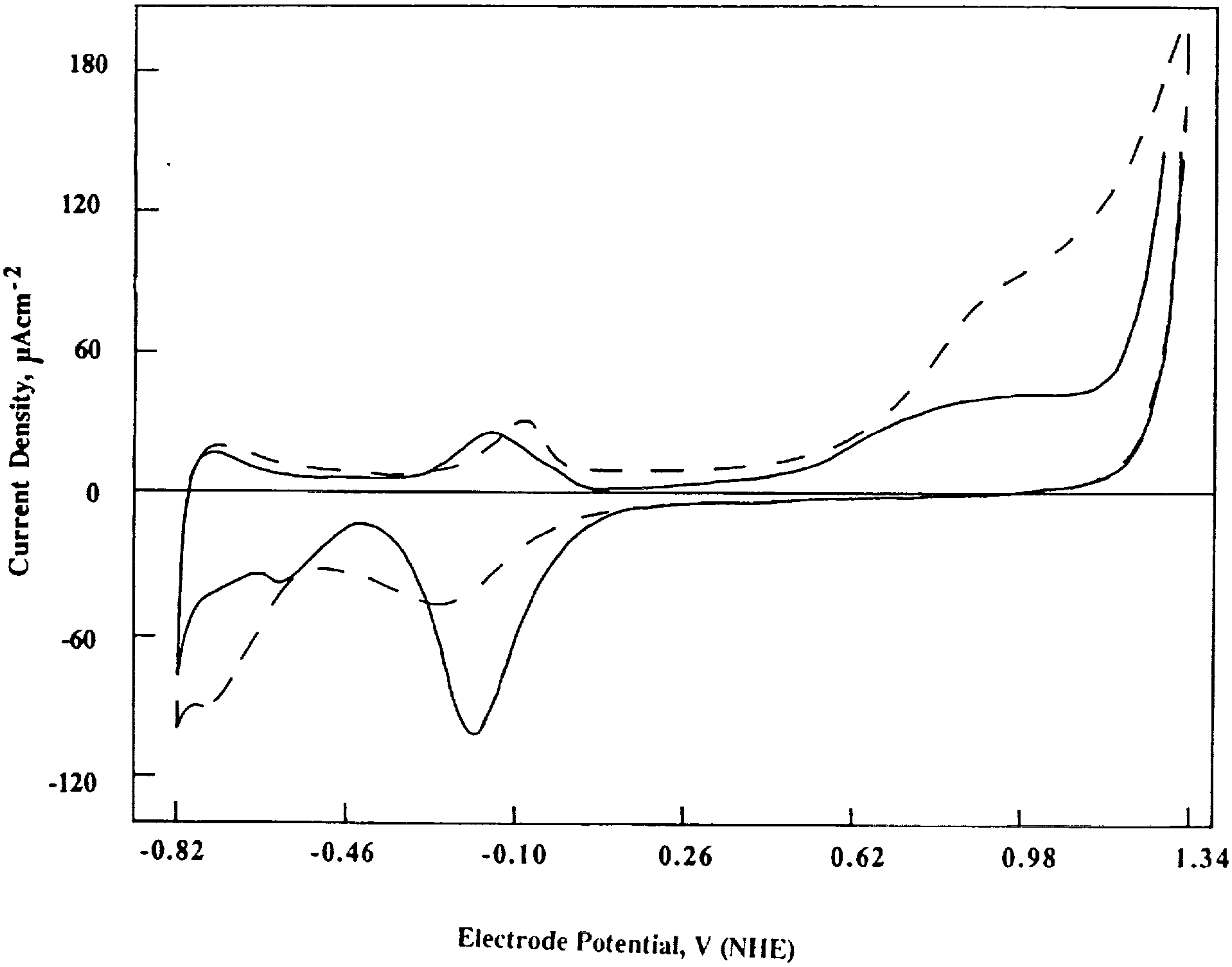


Figure 2 : Cyclic voltammogram in the absence (———) and in the presence (– – – –) of 0.1 M urea. The sweep rate was 15 mV/s and the electrolyte consisted of 1 M $NaClO_4$.

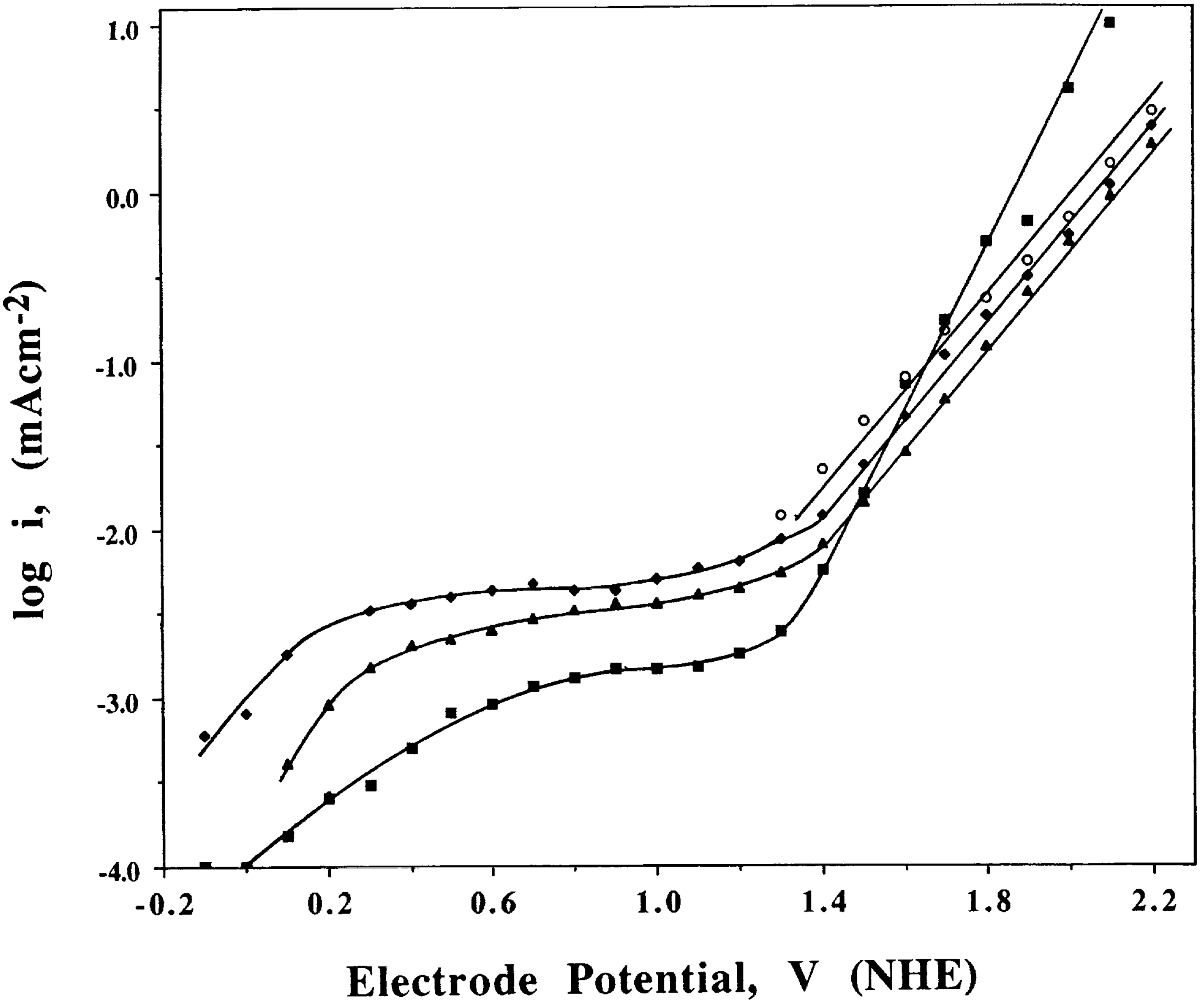


Figure 3 : Log i-V curve performed in the absence of urea (■) and in the presence of urea at concentrations of 1 M (▲) 3 M (◆) and 10 M (o) in 1 M $NaClO_4$ electrolyte.

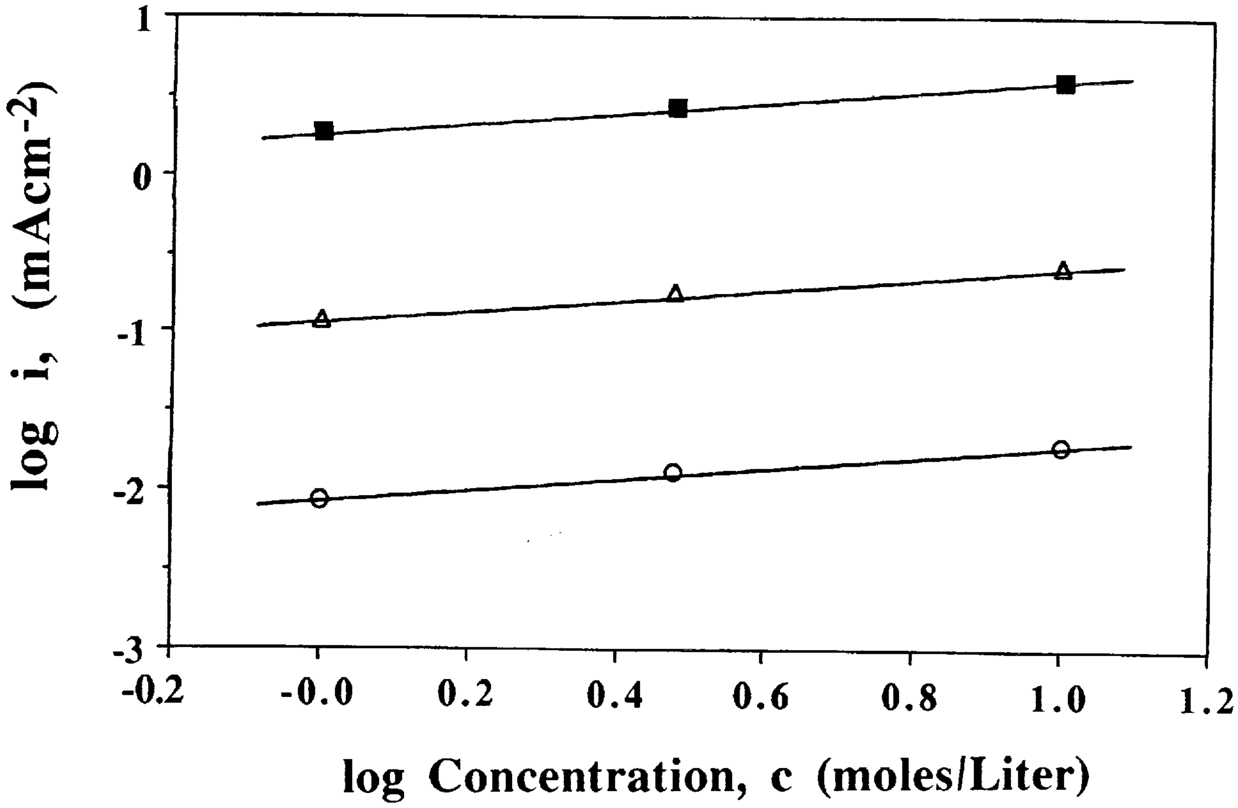


Figure 4 : Data from Figure 3 plotted as log i versus log urea concentration at 1.4 V(o) 1.8 V (Δ) and 2.2 V (■).

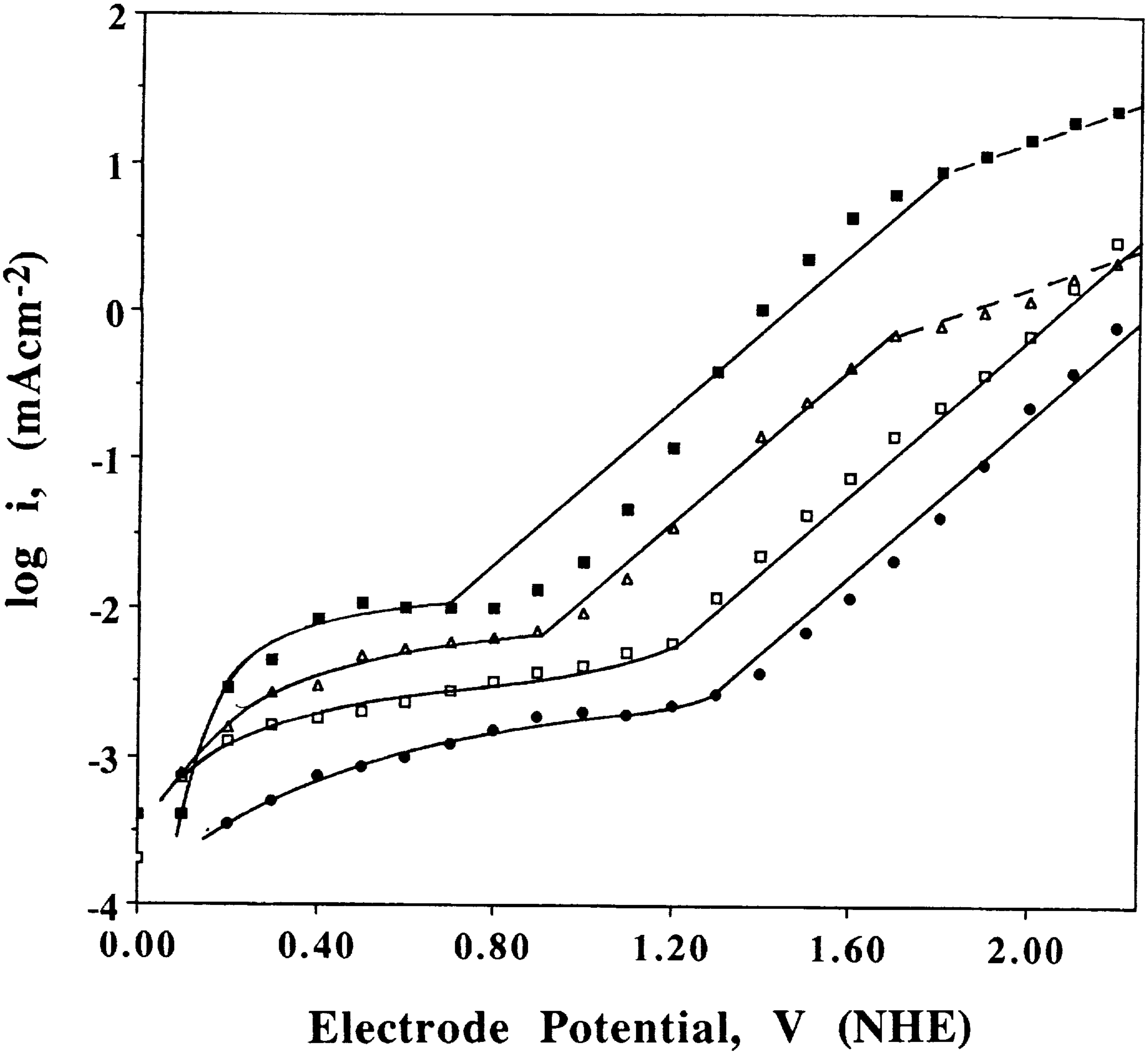


Figure 5 : Log i-V plot for 3 M urea at 15 (●) 30 (□) 60 (Δ) and 95 °C (■) in 1 M $NaClO_4$.

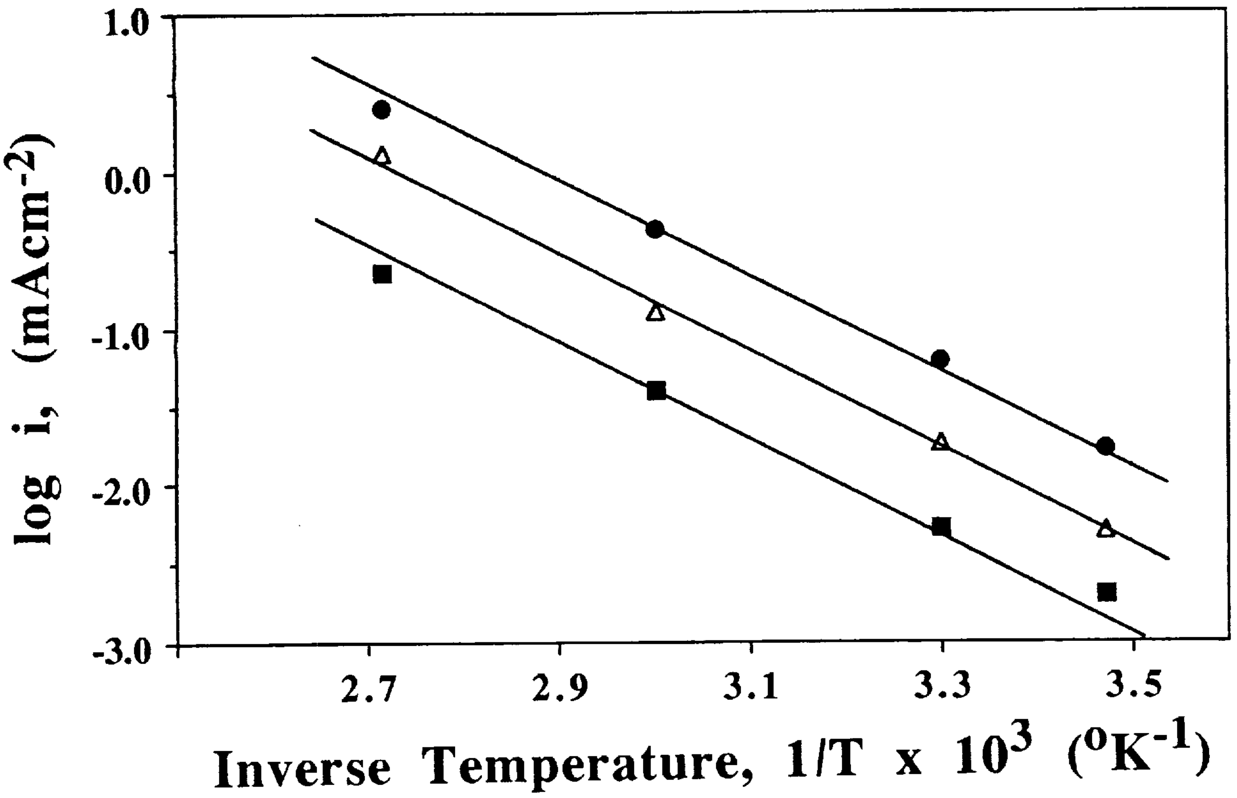


Figure 6 : Data from Figure 5 plotted as log i versus 1/T for 3 M urea at 1.2 (■) 1.4 (Δ) and 1.6 V (●) in 1 M $NaClO_4$.

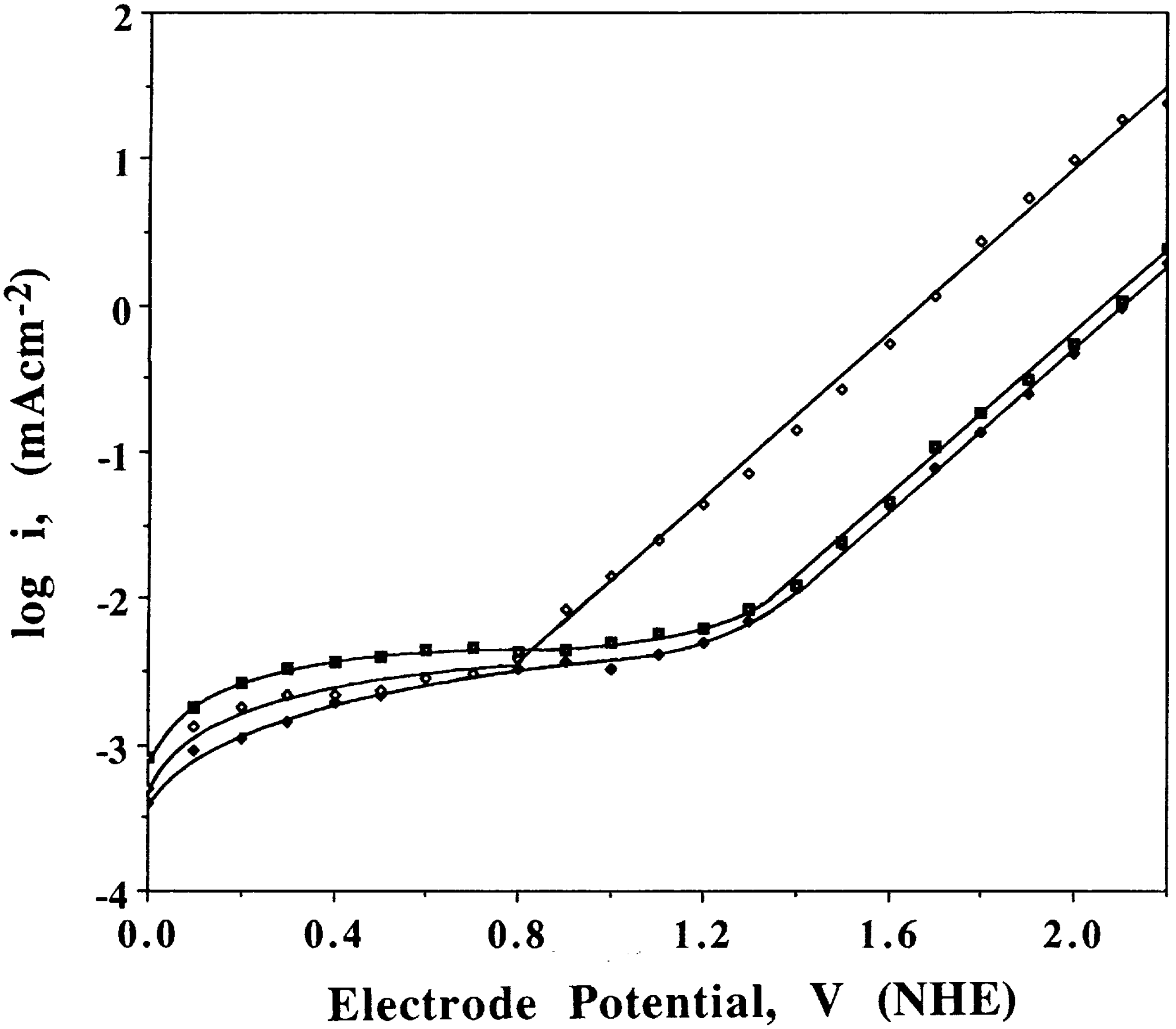


Figure 7 : Log i-V showing effect of pH for 3 M urea in 1 M $NaClO_4$ at 30°C. The pH was 6.4 (◆), 8.48 (■) and 13.8 (◇).

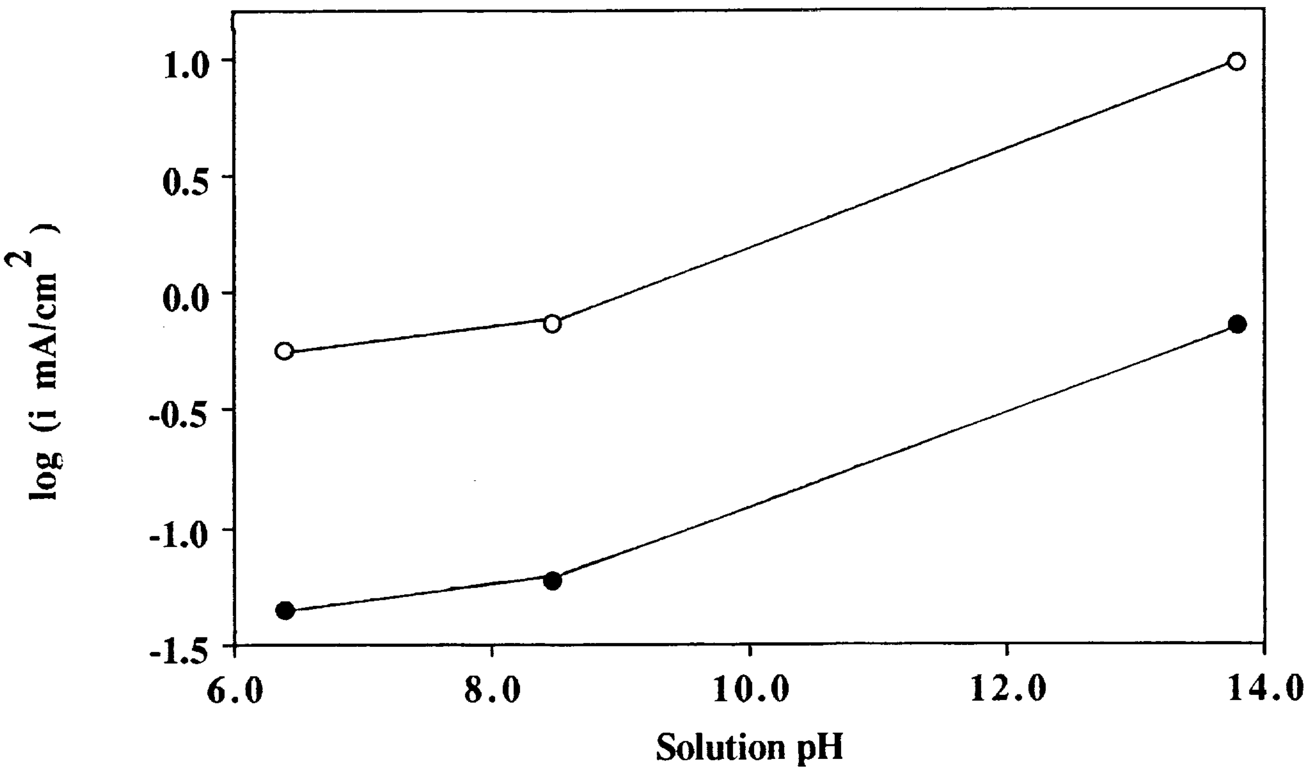


Figure 8 : Data from Figure 7 plotted as log i versus solution pH. The electrode potentials are 1.6V (●) and 2.0V (o).

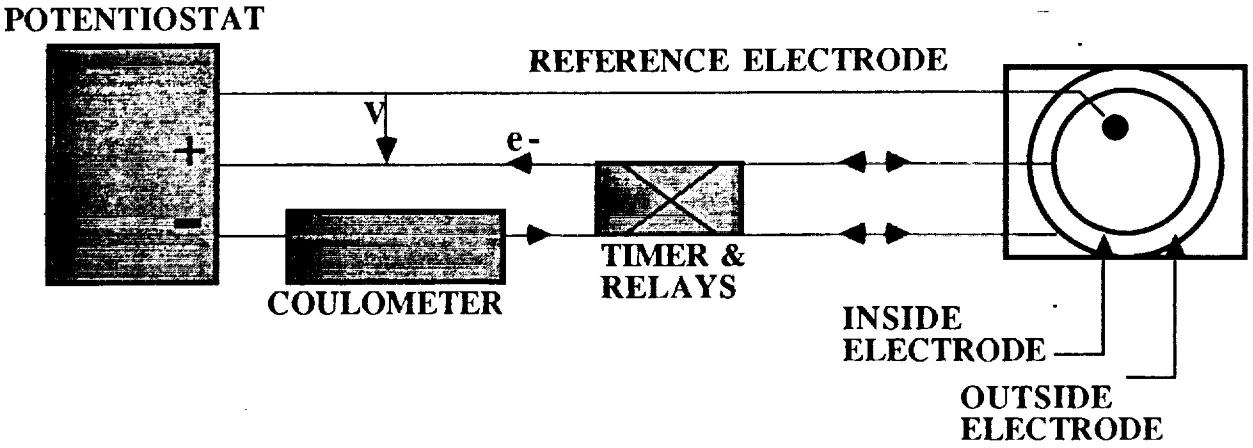

POTENTIOSTAT
REFERENCE ELECTRODE
V
e-
+
-
COULOMETER
TIMER &
RELAYS
INSIDE
ELECTRODE
OUTSIDE
ELECTRODE

Figure 9 : Test apparatus for periodic reversed pulse electrolysis.

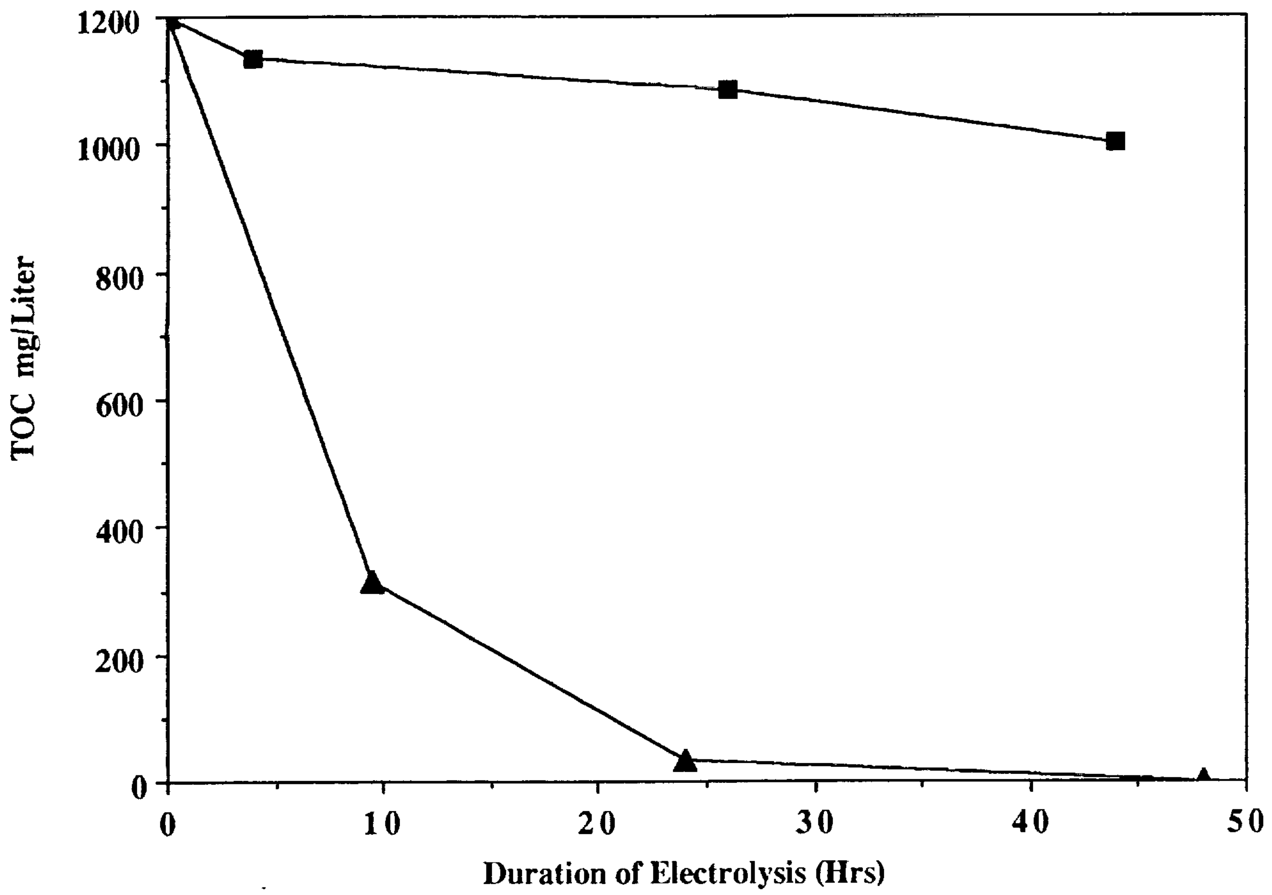


Figure 10 : Plot of TOC versus time for solutions containing urea at 6000 mg/Liter with (▲) and without (■) PRPE. The electrode potential was 1.4 V (NHE); the electrolyte was 1 M $NaClO_4$ at 30°C.

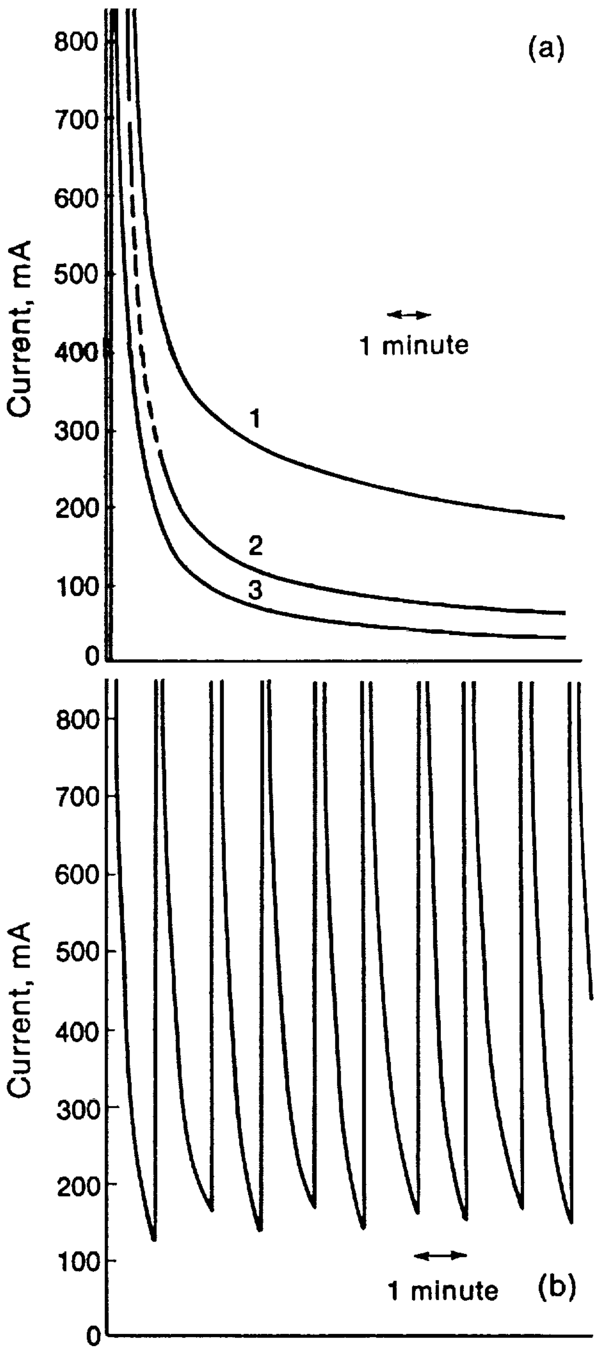


Figure 11 : The oxidation current for a urea solution without (a) and with (b) PRPE. In (a) 1 = 1.7V and 2 = 1.5V 3 = 1.3 V (NHE); (b) = 1.3 V (NHE).

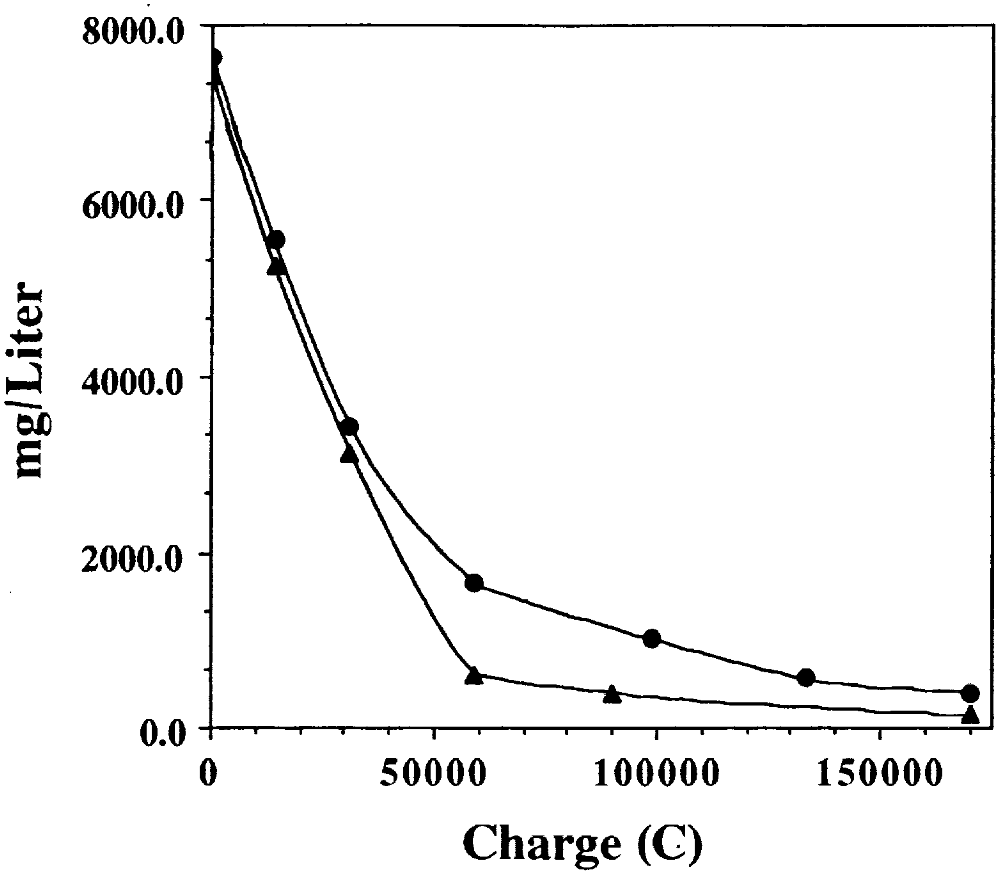


Figure 12 : PRPE of raw urine at 1.31 V (NHE). The PRPE frequency was 1 minute. TOC = ● , TKN = ▲.

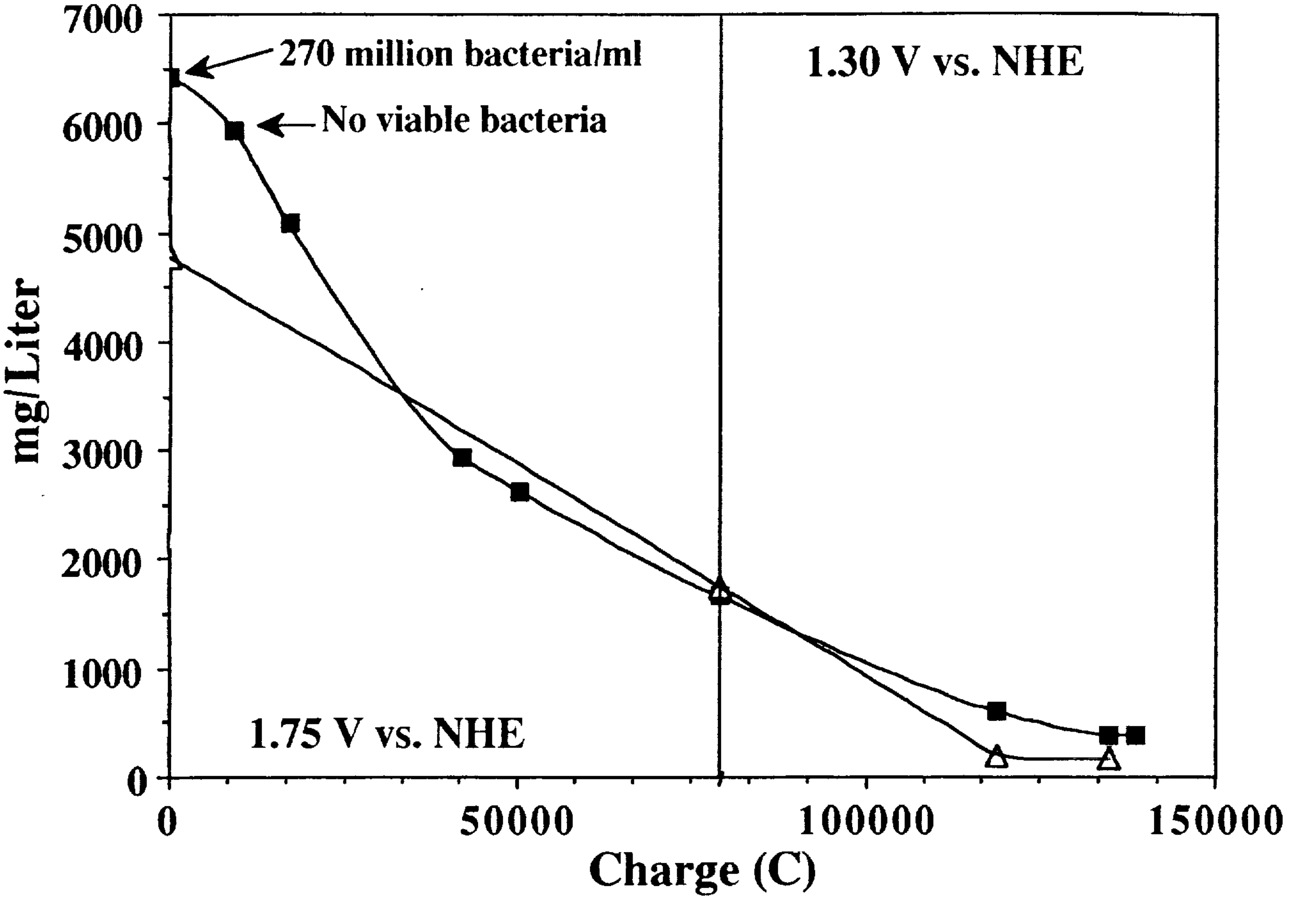


Figure 13 : Two stage raw urine oxidation and disinfection. TOC = ■ , TKN = Δ.

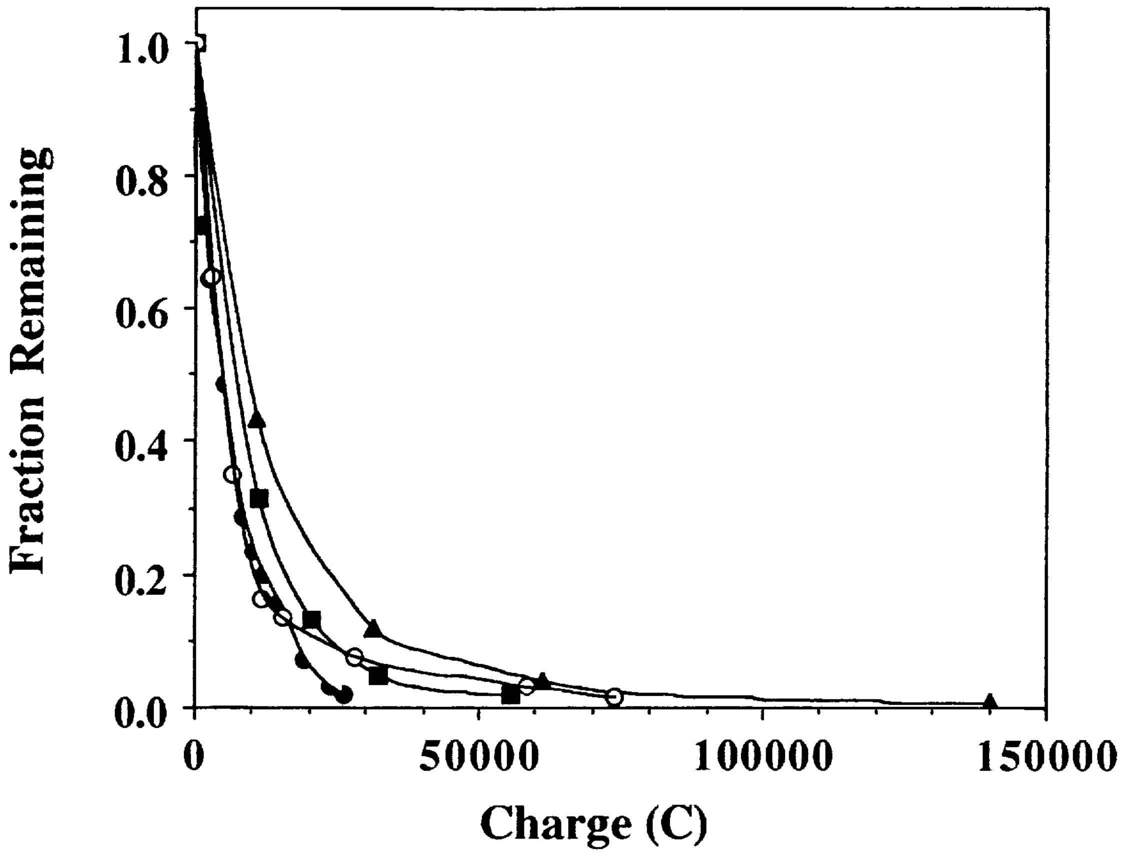
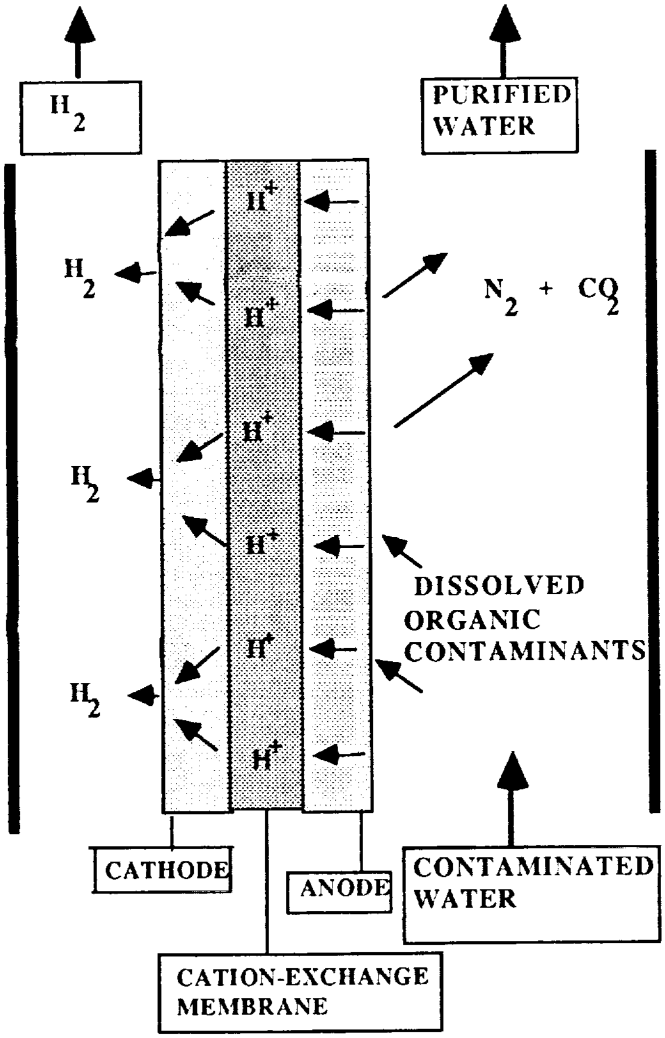


Figure 14 : Fraction remaining versus charge for simulated reclaimed water at an initial concentration of 56 ppm. The electrode potential was 1.2V (○) 1.4V (●) 1.6V (■) and 1.6V (▲) vs. NHE.


H2
PURIFIED WATER
H2
H2
H2
H+
H+
H+
H+
H+
H+
N2 + CO2
DISSOLVED ORGANIC CONTAMINANTS
CATHODE
ANODE
CONTAMINATED WATER
CATION-EXCHANGE MEMBRANE

TYPICAL DISSOLVED ORGANIC CONTAMINANTS

Acetic Acid: $CH_3COOH + 2H_20 \rightarrow 2CO_2 + 4H_2$

Benzoic Acid : $C_6H_5COOH + 12H_2O \rightarrow 7CO_2 + 15H_2$

Octanoic Acid : $CH_3(CH_2)_6COOH + 14H_2O \rightarrow 8CO_2 + 22H_2$

Urea: $NH_2CONH_2 + H_2O \rightarrow CO_2 + N_2 + 3H_2$

ORGANIC OXIDATION REACTIONS

Figure 15 : Design concept of a membrane-based electrolyzer.